Synthesis and Characterization of Fluoropropyl POSS

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Report Documentation Page

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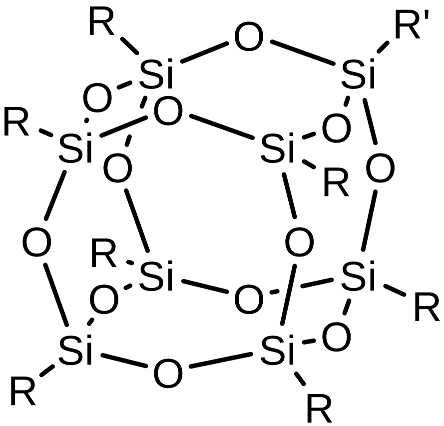
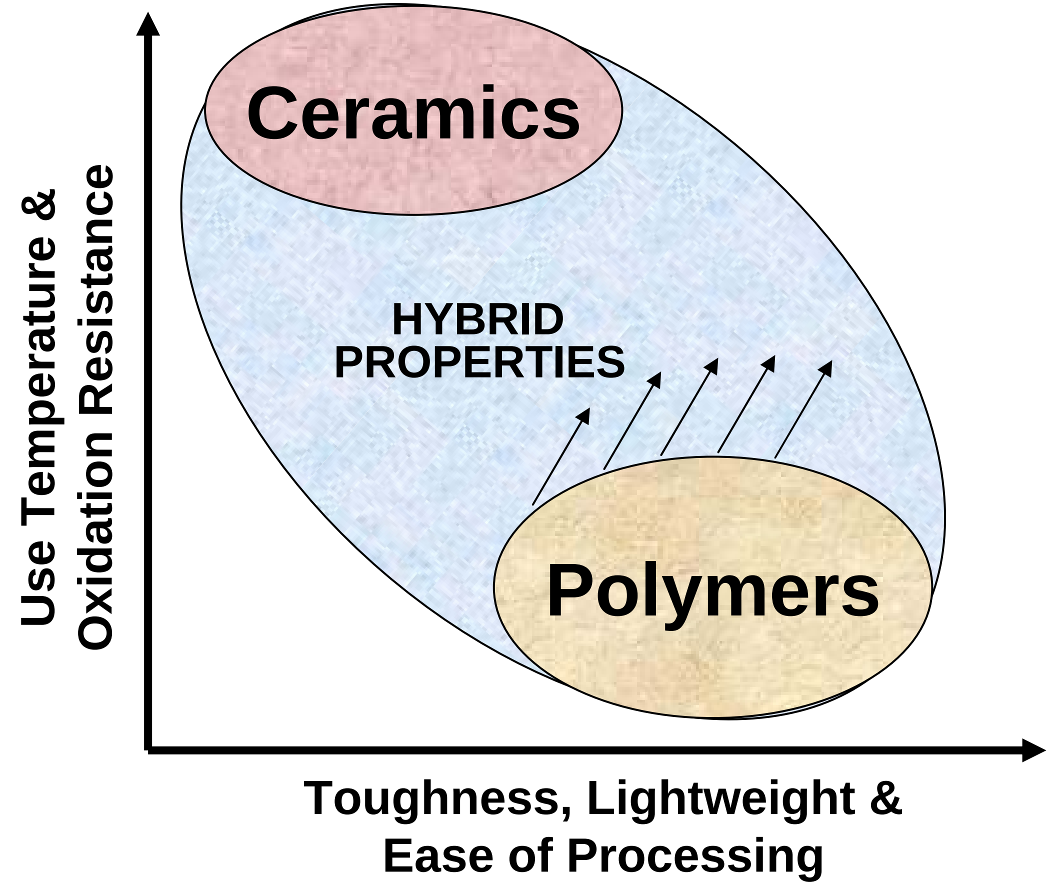
Outline

- **POSS**
- **FluoroPOSS Synthesis**
- **Fluoropropyl POSS Synthesis**
- **Conclusion**



Hybrid inorganic/organic polymers

Goal: Develop High Performance Polymers that REDEFINE material properties

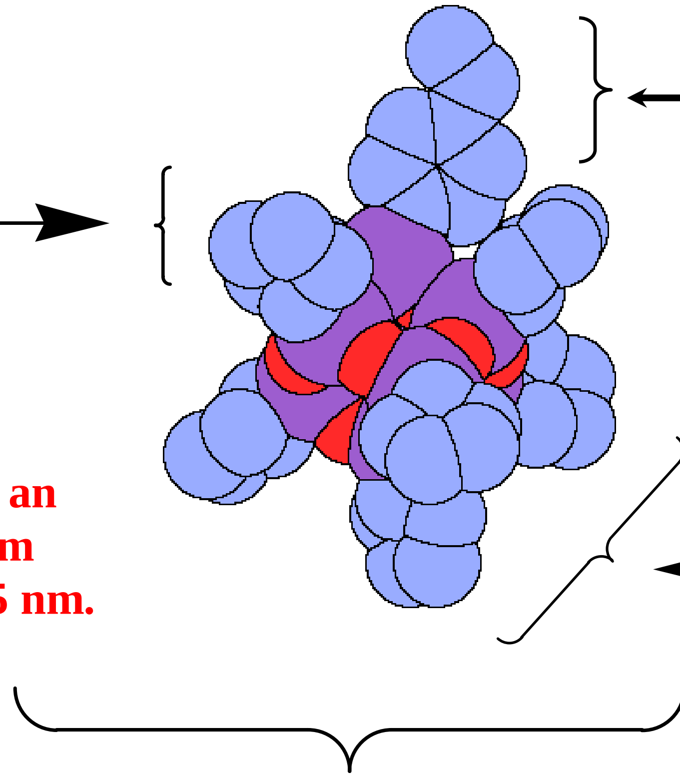


- **Hybrid plastics bridge the differences between ceramics and polymers**

Anatomy of a POSS nanostructure

May possess one or more functional groups suitable for polymerization or grafting.

Nonreactive organic (R) groups for solubilization and compatibilization.



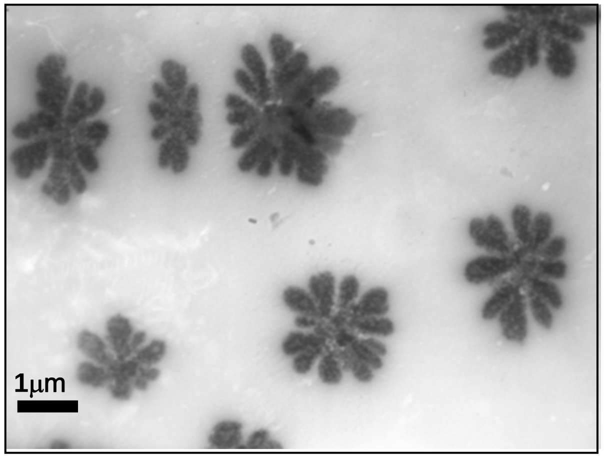
Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm.

Thermally and chemically robust hybrid (organic-inorganic) framework.

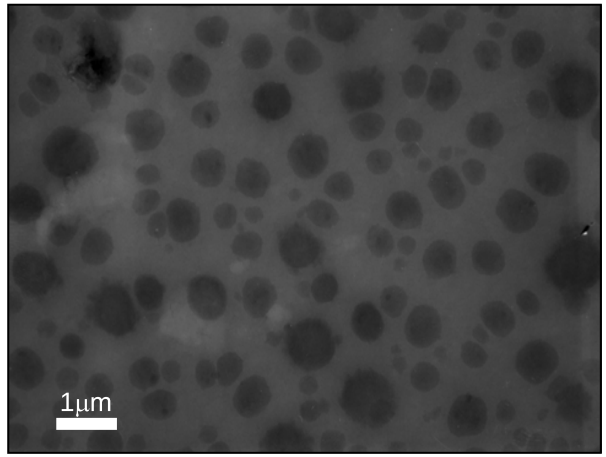
Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

Importance of R groups:
Affect compatibility with polymer matrix

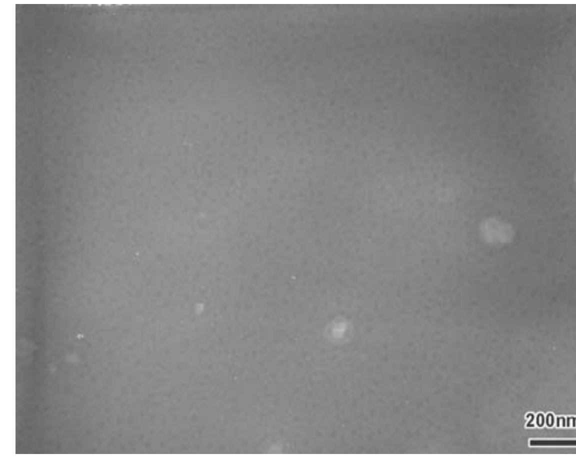
50 Wt % POSS Blends in 2 Million MW PS



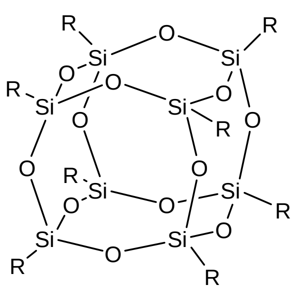
Domain Formation



Partial Compatibility

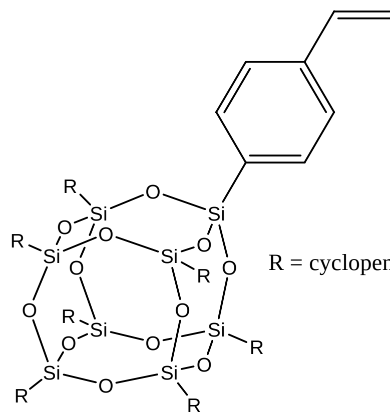


Complete Compatibility



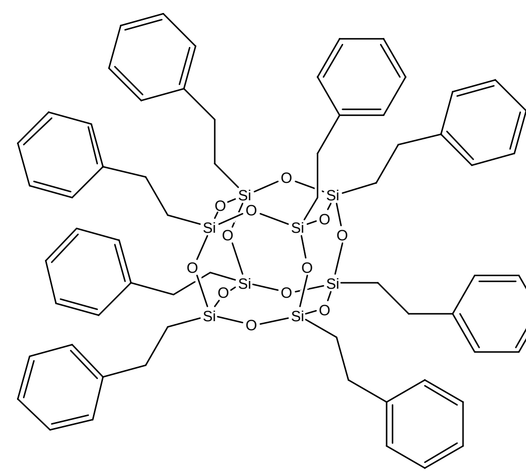
R = cyclopentyl

Cp_8T_8



R = cyclopentyl

Cp_7T_8Styryl



Phenethyl$_8$T$_8$

Blanski, et al., *Polymer Preprints*, **2000**. 41(1): p. 585.

Fluoropolymer seals

Integrated High Payoff Rocket Propulsion Technology (IHPRPT) Program

- National program focused by OSD/DDR&E/AT and coordinated with AF, NASA, Navy, Army, and industry.
- Goal-oriented technology development program for rocket propulsion.
    - Double the performance of rocket propulsion systems over current state of the art.
    - Decrease the cost of access to space for commercial and military sectors.

- Fluoropolymers are used in many seal applications in liquid rocket engines
    - Polychlorotrifluoroethylene (PCTFE)
    - Fluorinated Ethylene/Propylene (FEP)
- Fluoropolymer research is designed to:
    - Improve Isp
    - Improve Thrust to Weight ratio
    - Reduce Support Costs
    - Lengthen Mean Time Between Removal

Targeted shortfalls

Mechanical Problems

- During operation, wear ring seals preventing propellant flow from bypassing the impeller blades in the SSME turbopump warp, causing an estimated 1.5 sec loss of delivered I_{sp}.
  (I_{sp} and Thrust to Weight)

  1.5 sec I_{sp} x 3 SSMEs x 1000 lb payload/sec I_{sp} x $8,000/lb payload =
  $36,000,000 per launch

- Creep (cold flow of materials under load) causes the deformation of fluoropolymer seals in LREs, limiting their functional use time. (Mean Time Between Removal)

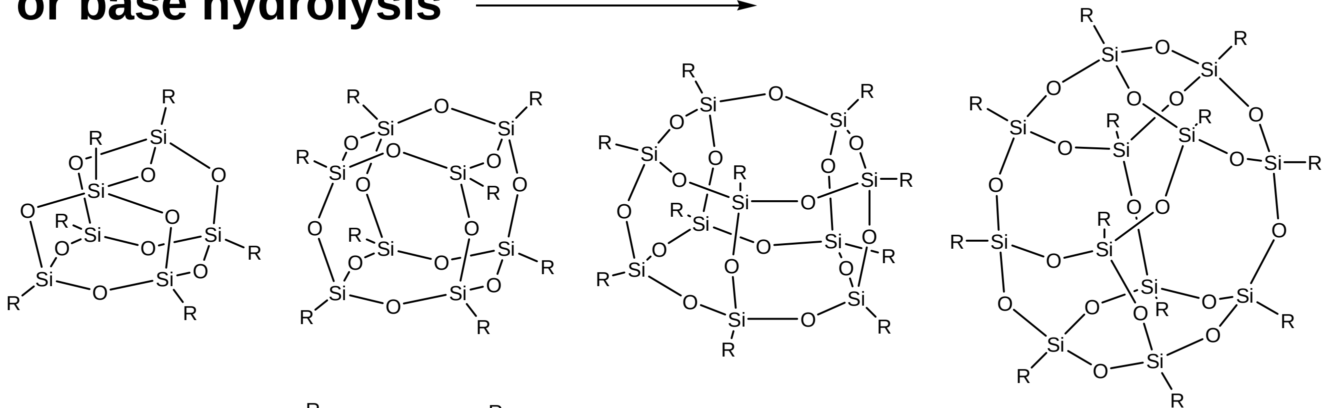
Surface Property Problems

- Fuel wetting of fluoropolymer seals allows fuel to leak past seals. A costly nitrogen purge is necessary to prevent fuel contact with oxidizer. (Reduce Support Costs and Thrust to Weight)

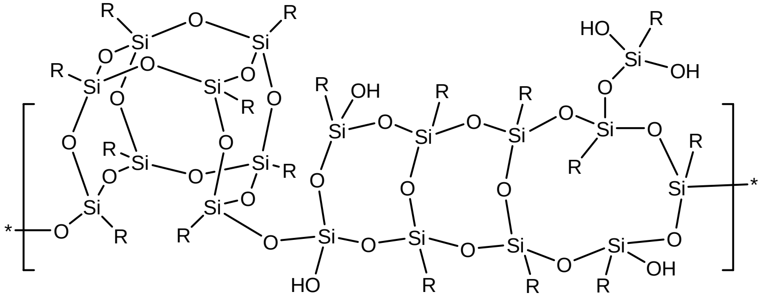
POSS synthesis

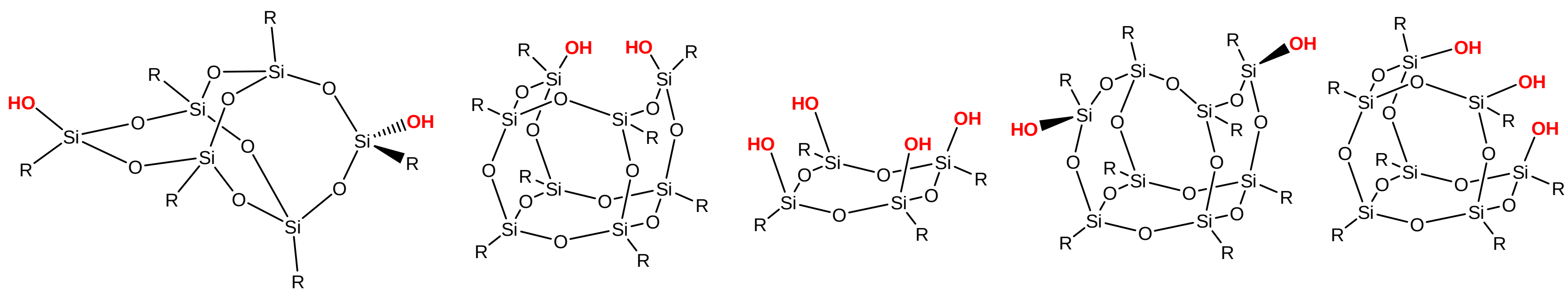
$RSiX_3$ acid or base hydrolysis →

Blendables



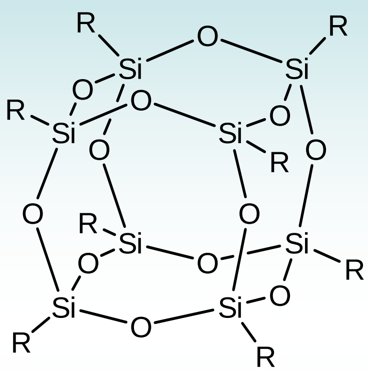
Resin



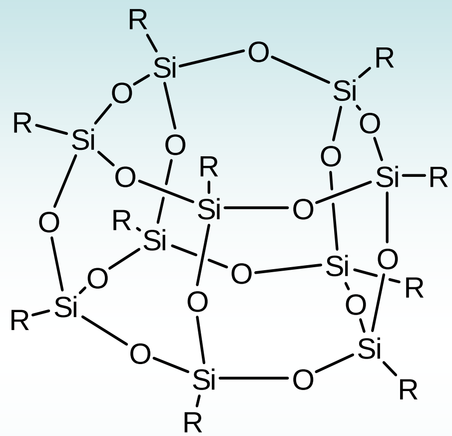


Incompletely condensed cages

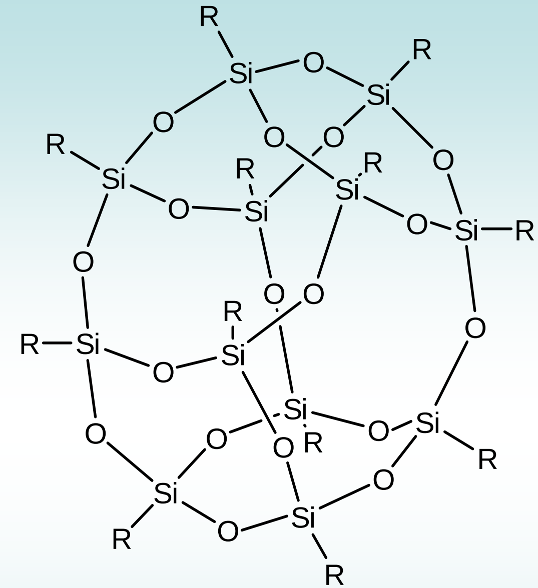
Typical isomers produced



T_8



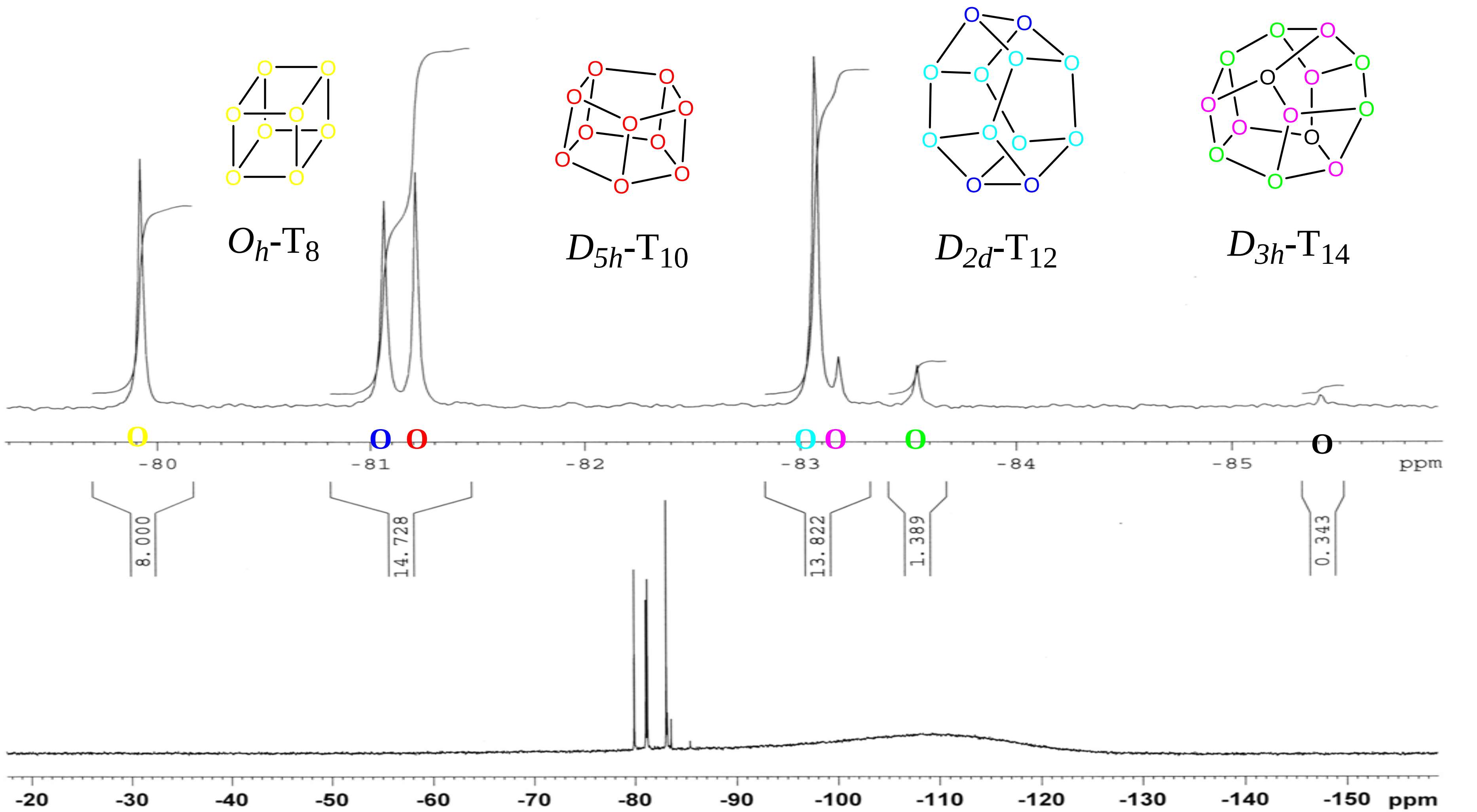
T_{10}



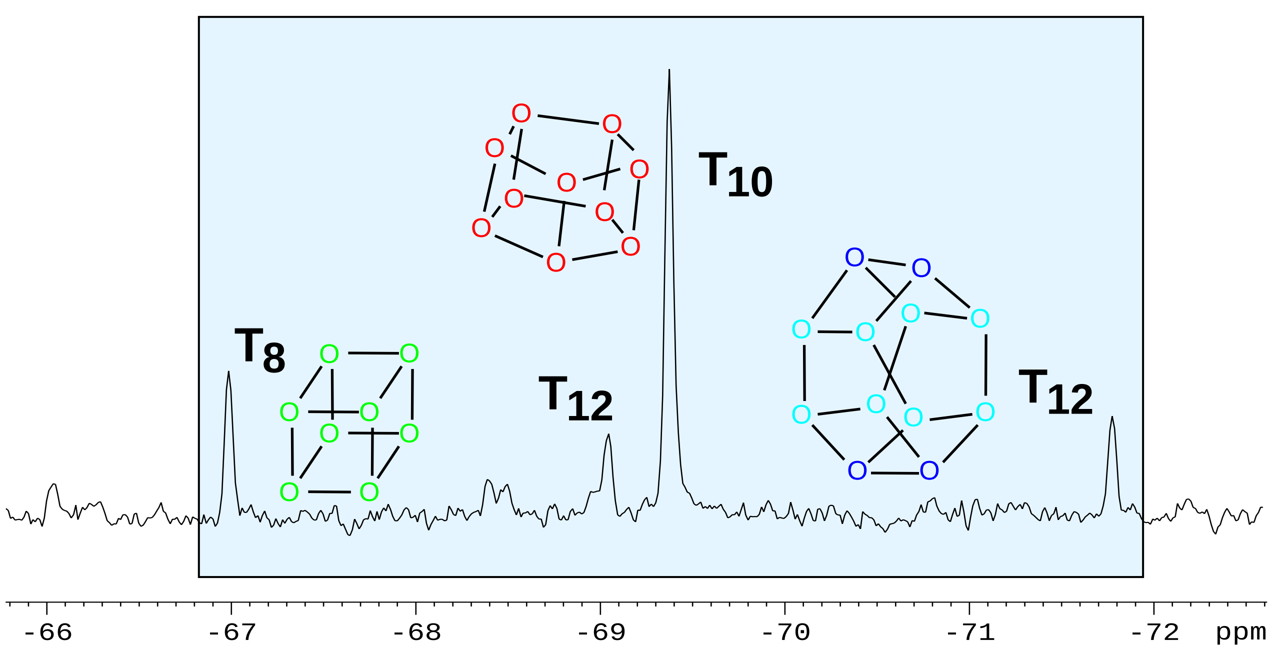
T_{12}

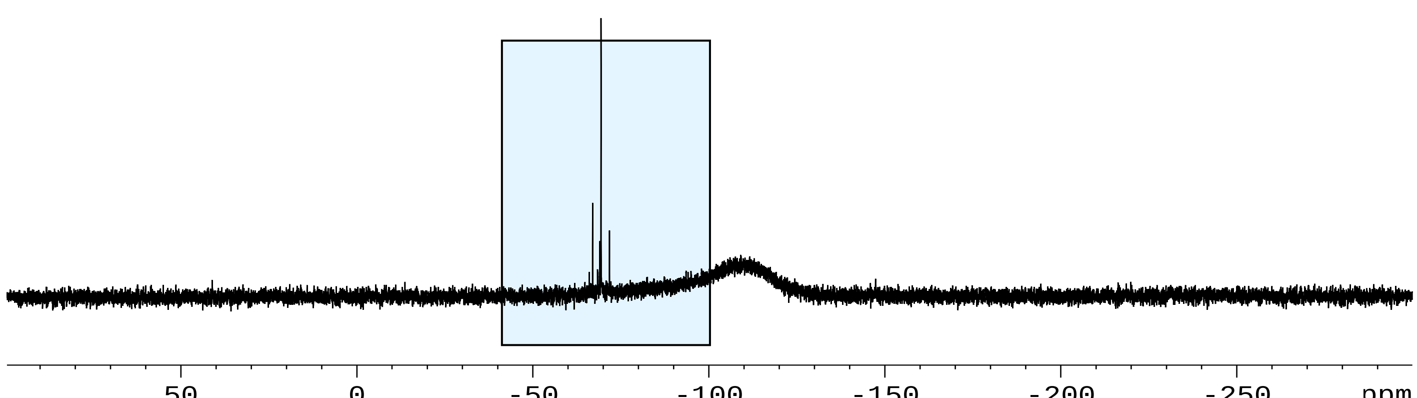
Most common compounds found in a cage mixture

29Si NMR spectrum of cage mixture



29Si NMR of Fluorohexyl cage mixture



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RG                  11585.2
DW                   21.000 usec
DE                     6.00 usec
TE                    300.0 K
D1               8.00000000 sec
d11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                   29Si
P1                    10.00 usec
PL1                   -3.00 dB
SFO1             59.6214106 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                  120.00 dB
PL12                  20.00 dB
SFO2            300.1312005 MHz

F2 - Processing parameters
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GB                        0
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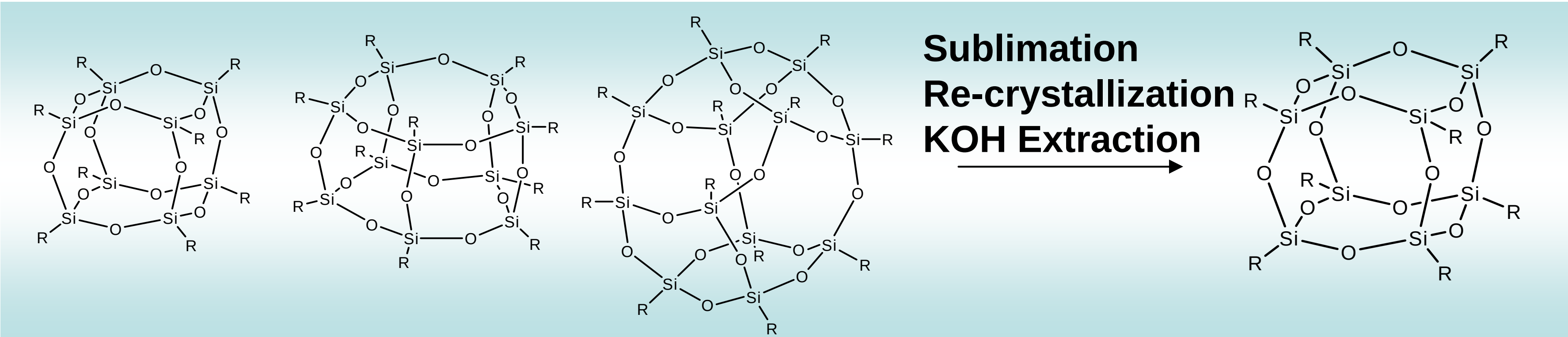
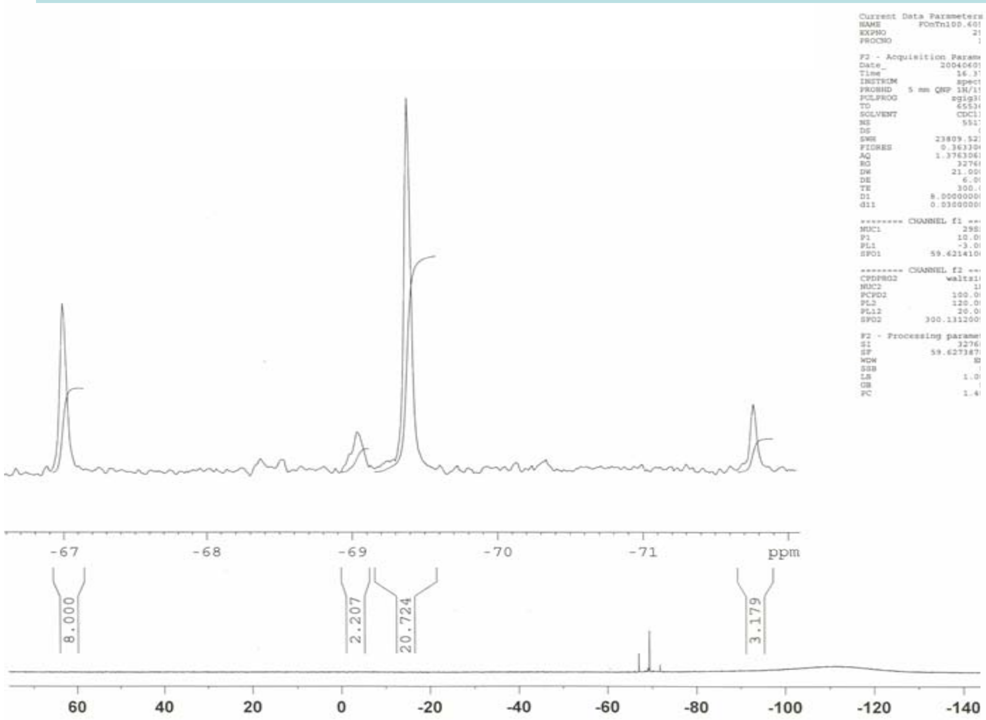
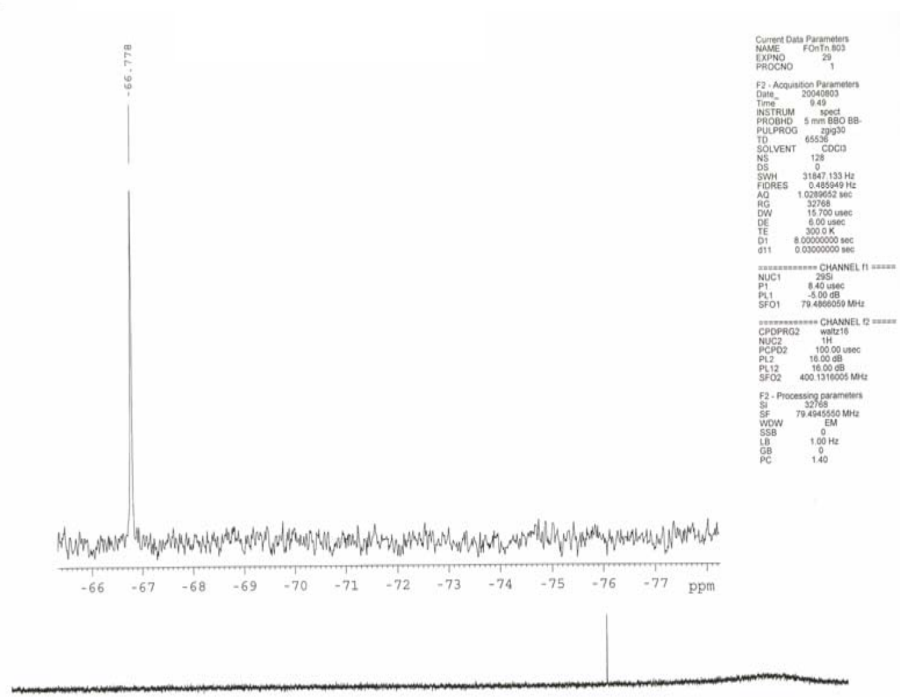
```

Redistribution reaction

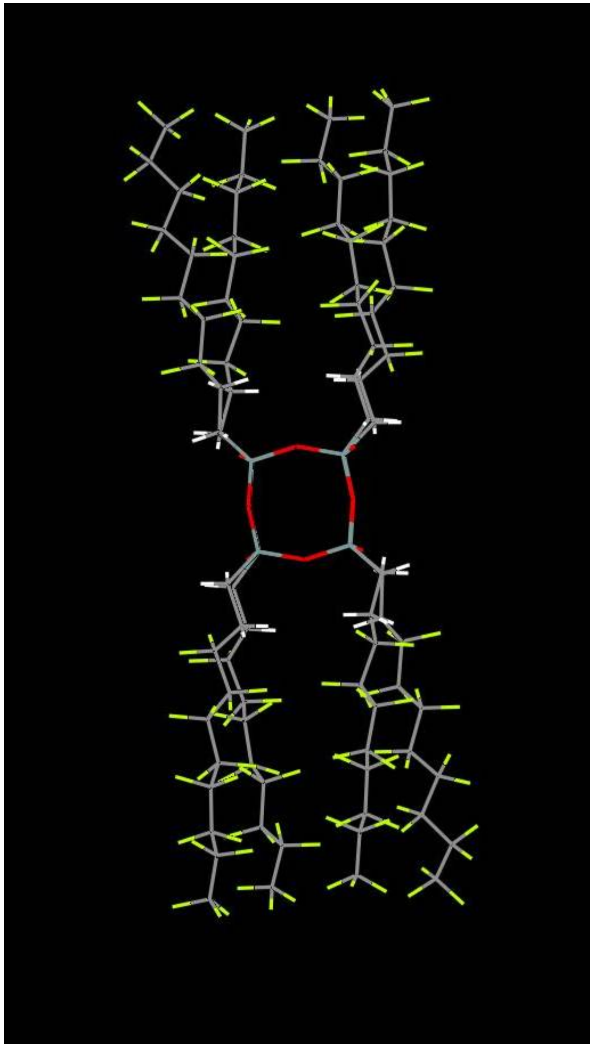




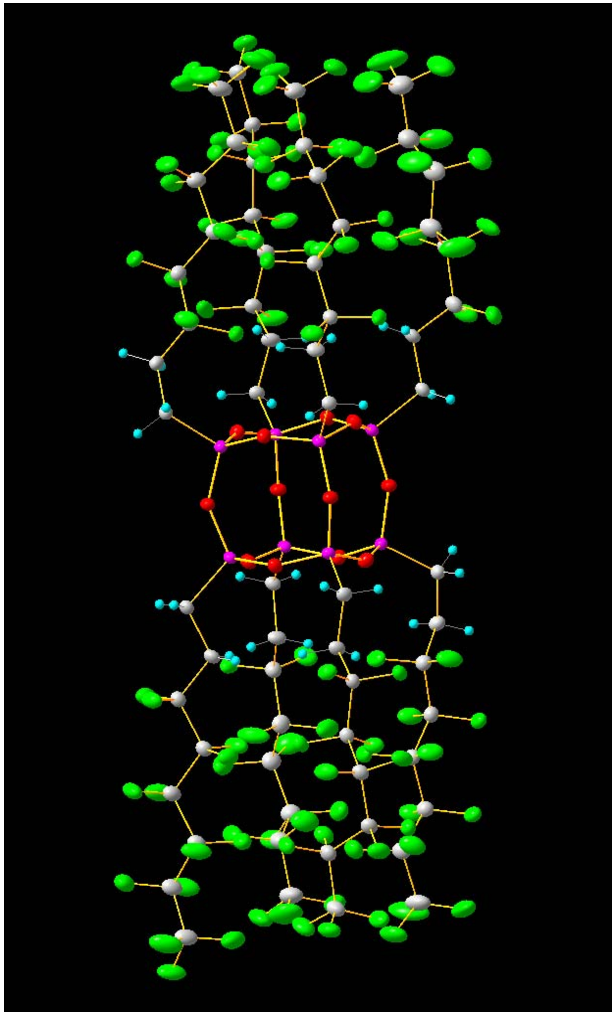


Distribution A: Approved for public release; distribution unlimited

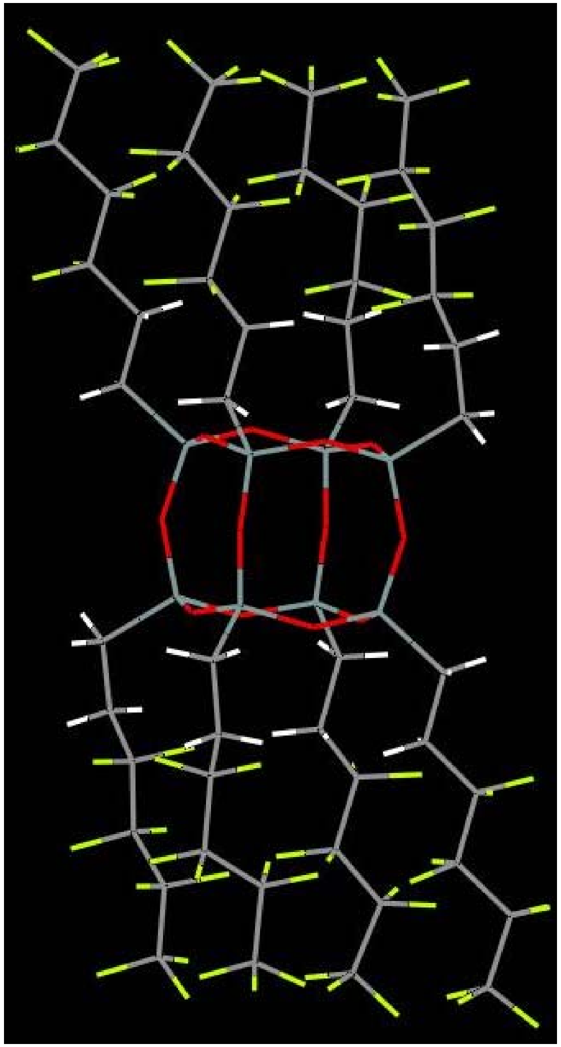
Crystal structures of FluoroPOSS$_8$T$_8$



Decyl-

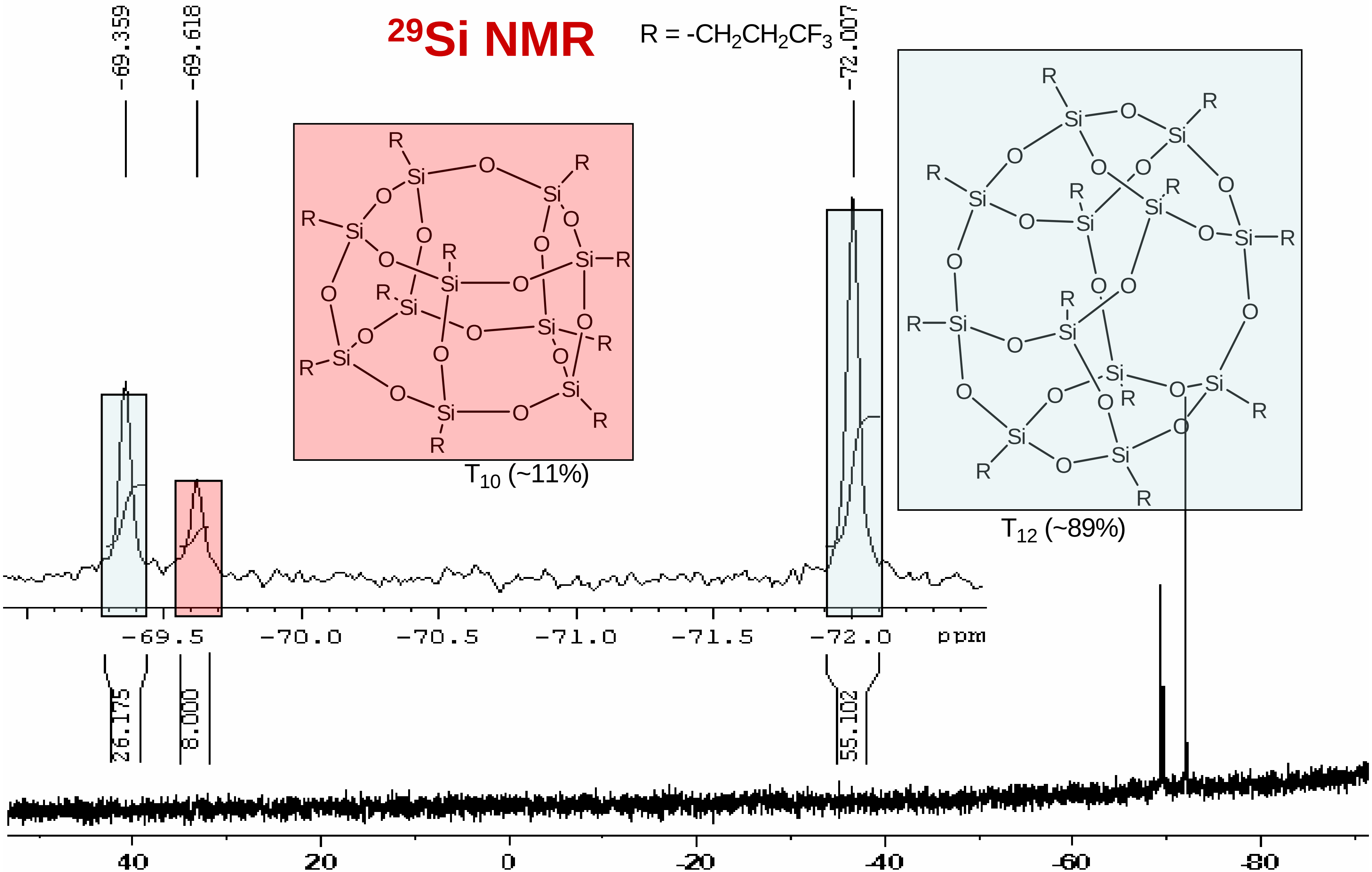


Octyl-



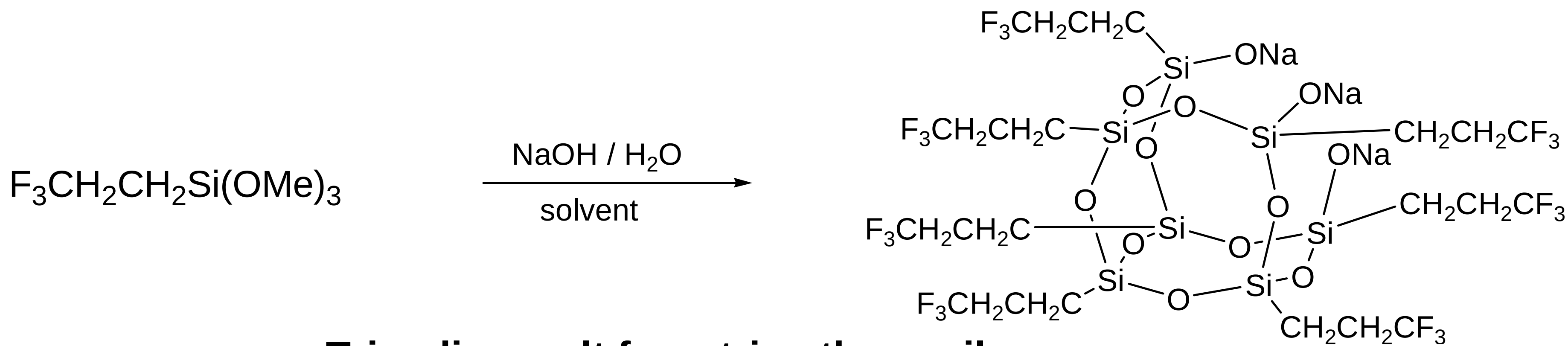
Hexyl-

$Fluoropropyl_nT_n$

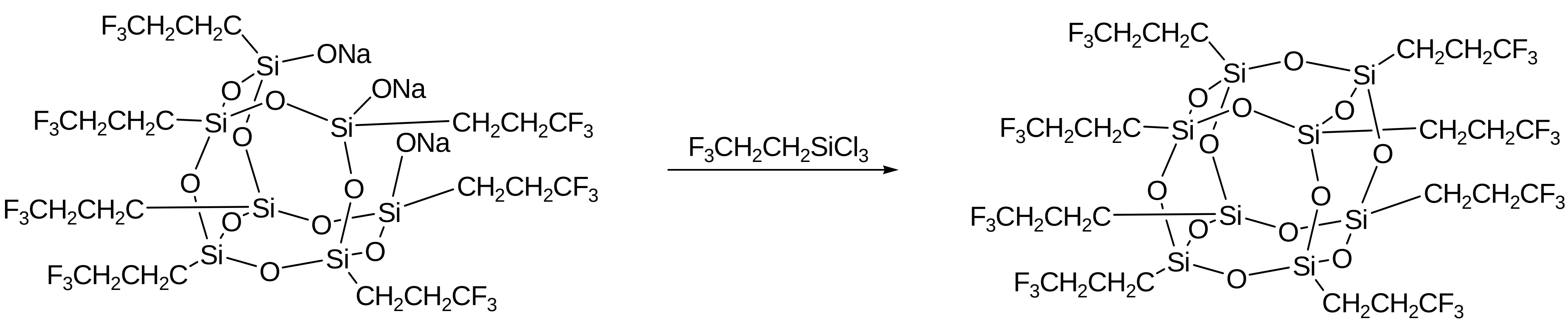


Distribution A: Approved for public release; distribution unlimited

Fluoropropyl8T8

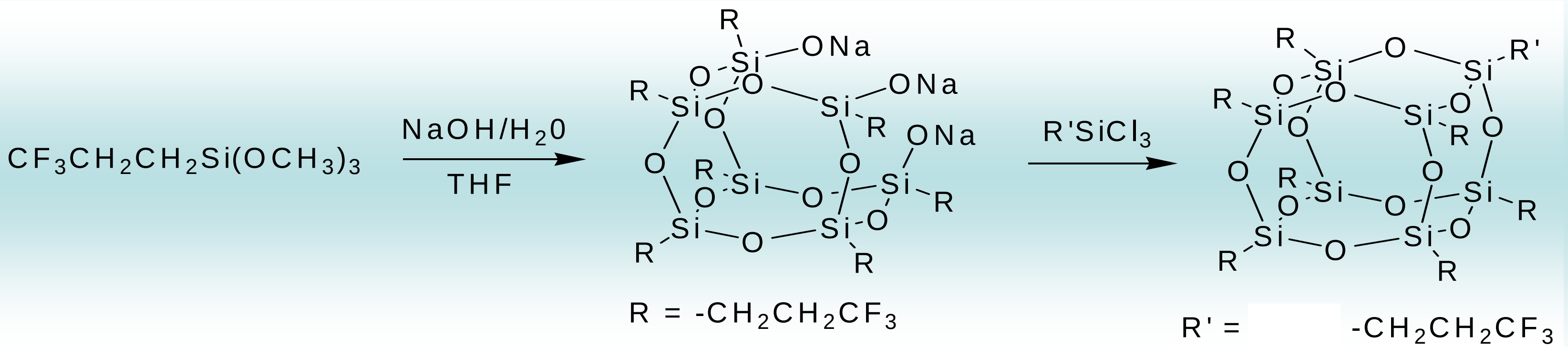


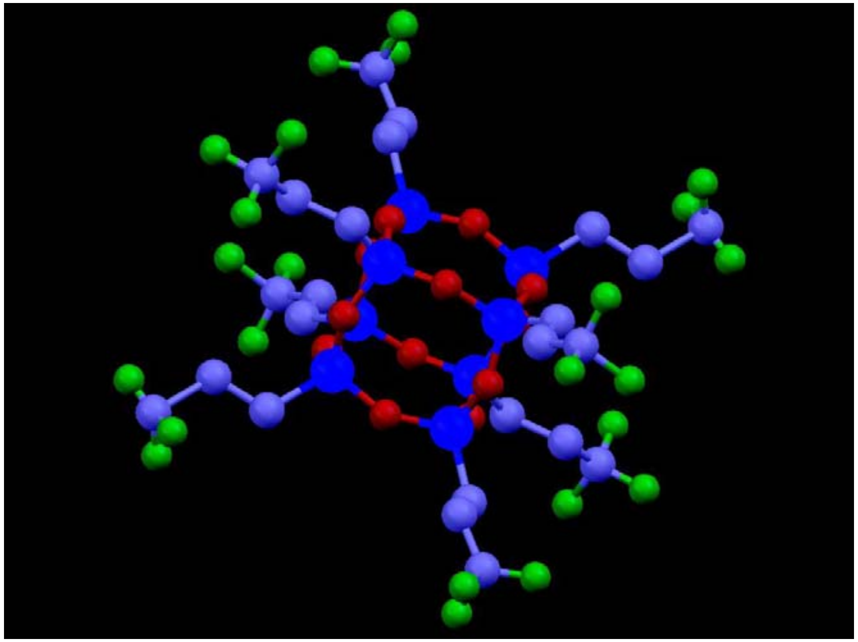
Trisodium salt from trimethoxy silane

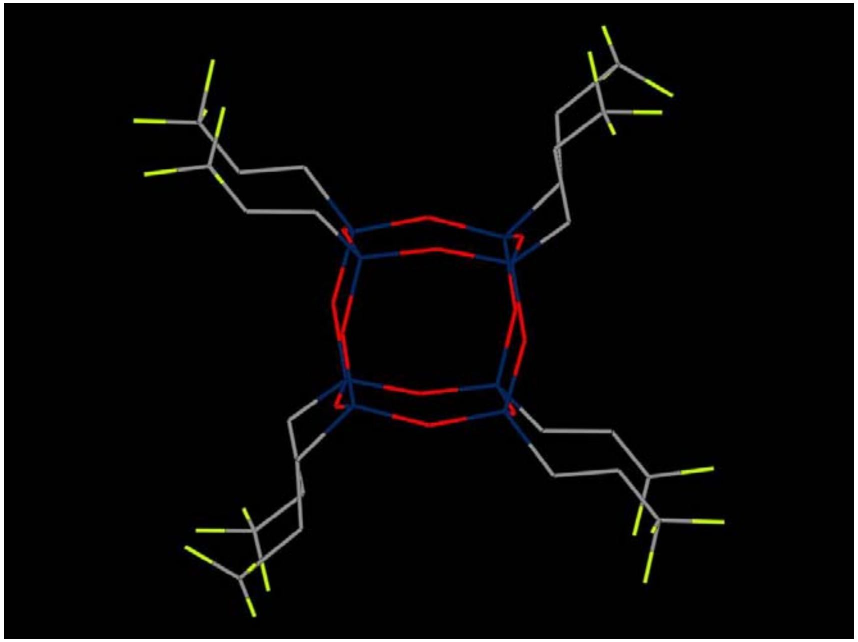


T_8 from trisodium salt

Trifluoropropyl T_8 POSS

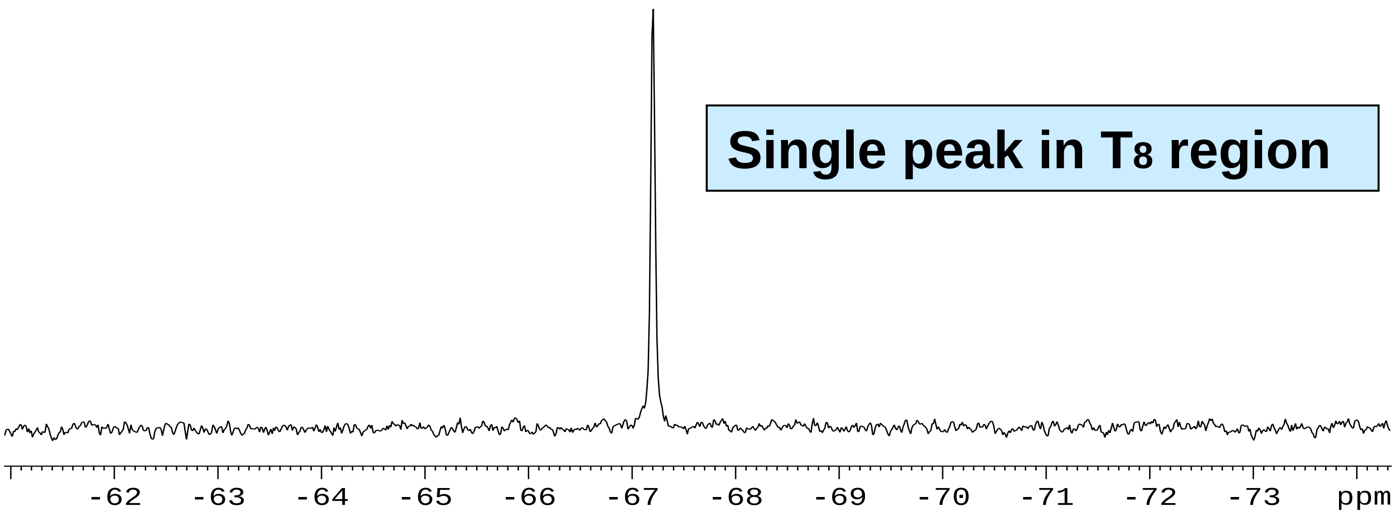






29Si NMR Trifluoropropyl POSS

Corner capped Trifluoropropyl POSS



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FIDRES	0.363304	Hz
AQ	1.3763061	sec
RG	32768	
DW	21.000	usec
DE	6.00	usec
TE	300.0	K
D1	8.00000000	sec
d11	0.03000000	sec

======== CHANNEL f1 ========

NUC1	29Si	
P1	10.00	usec
PL1	-3.00	dB
SFO1	59.6214106	MHz

======== CHANNEL f2 ========

CPDPRG2	waltz16	
NUC2	1H	
PCPD2	100.00	usec
PL2	120.00	dB
PL12	20.00	dB
SFO2	300.1312005	MHz

F2 - Processing parameters

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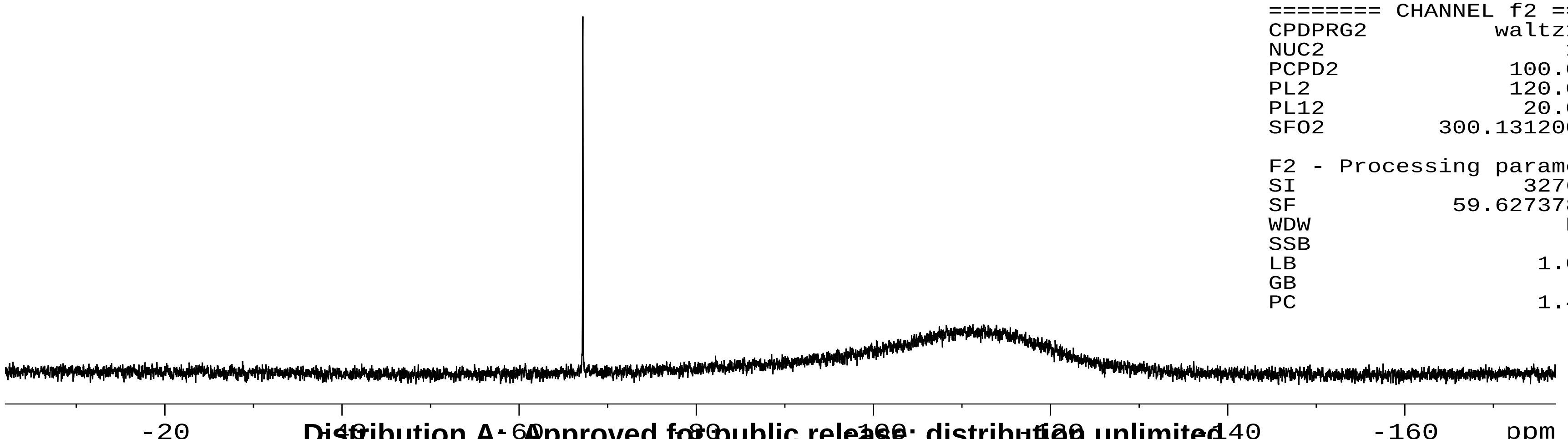
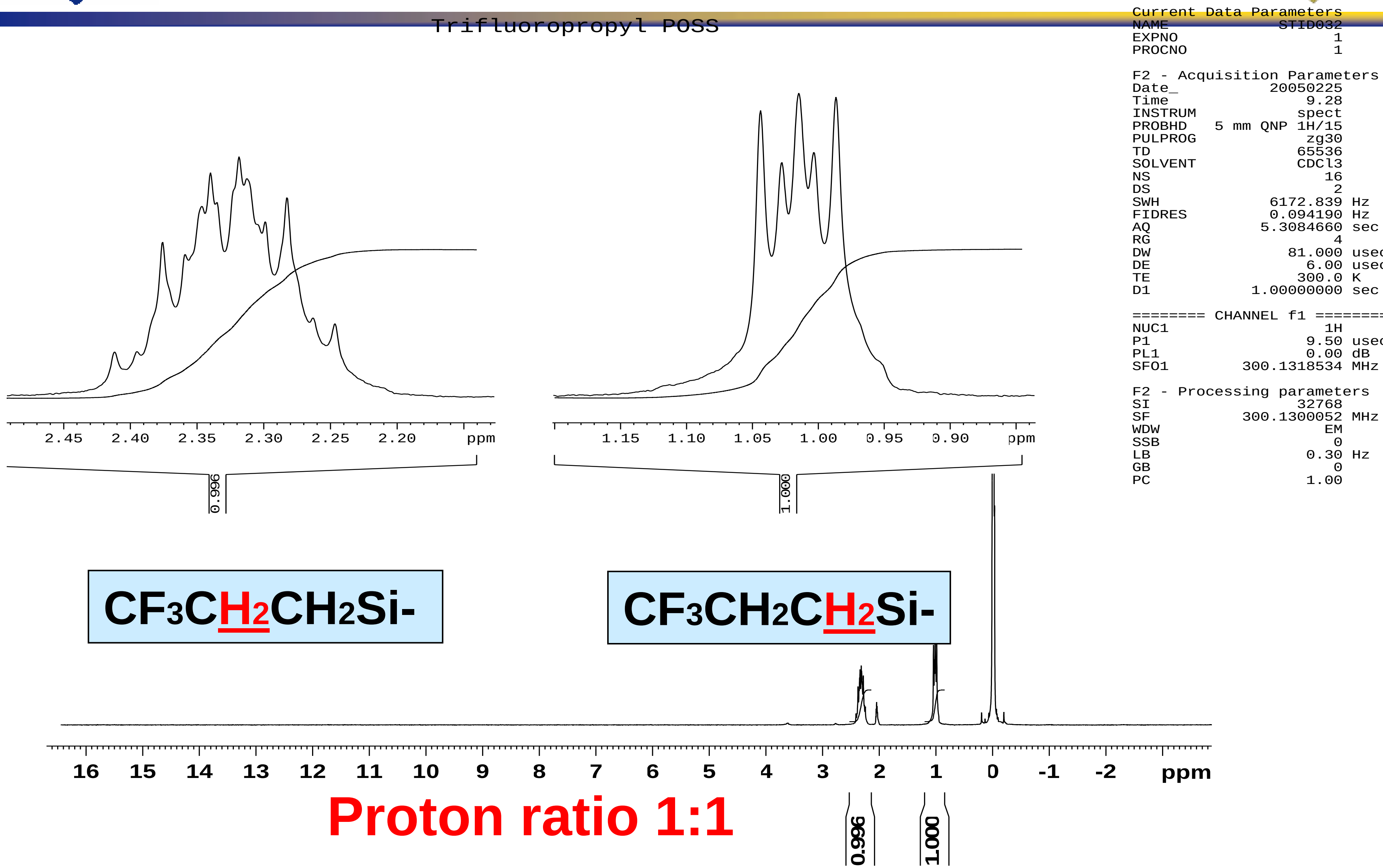
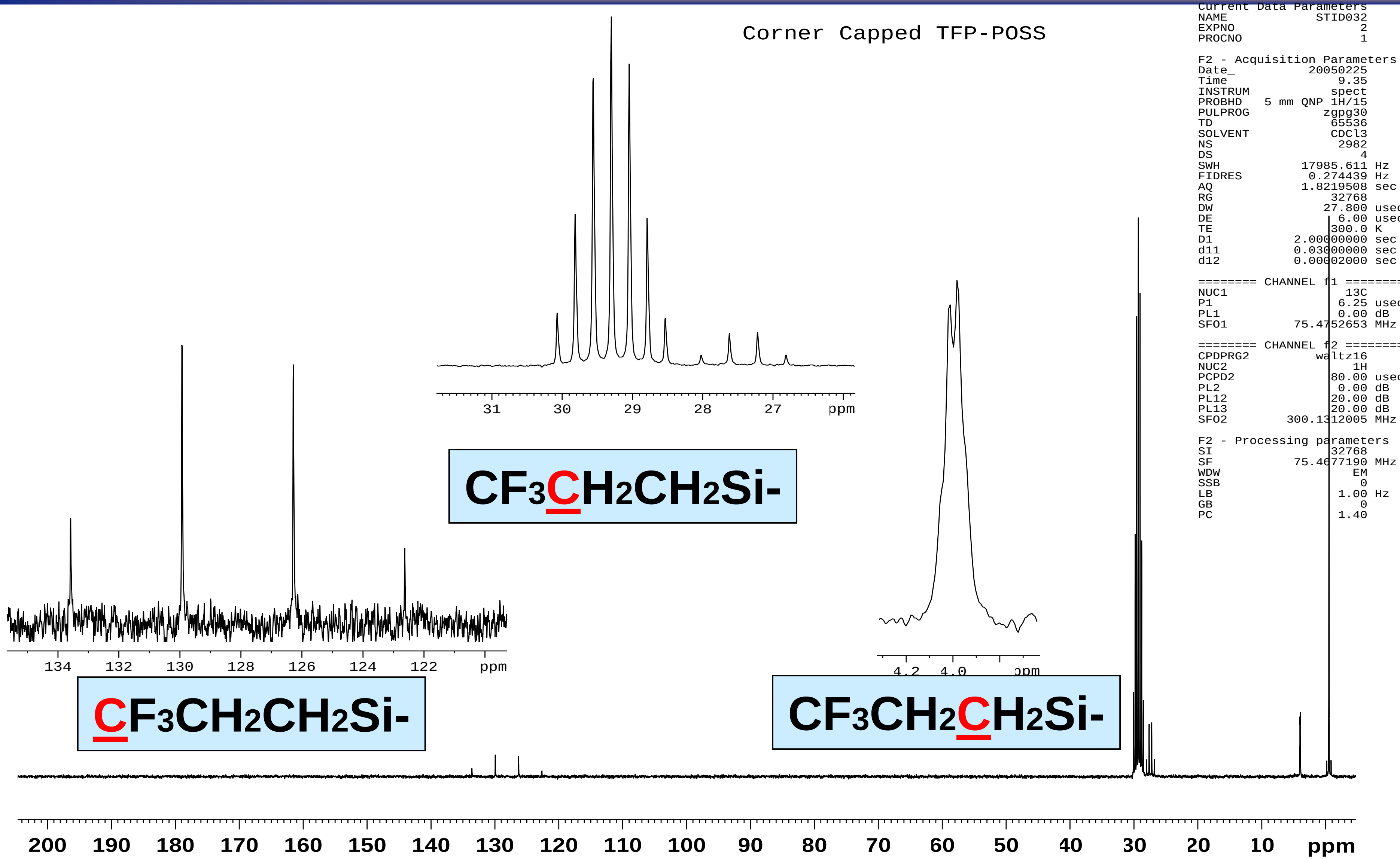


1H NMR Trifluoropropyl POSS

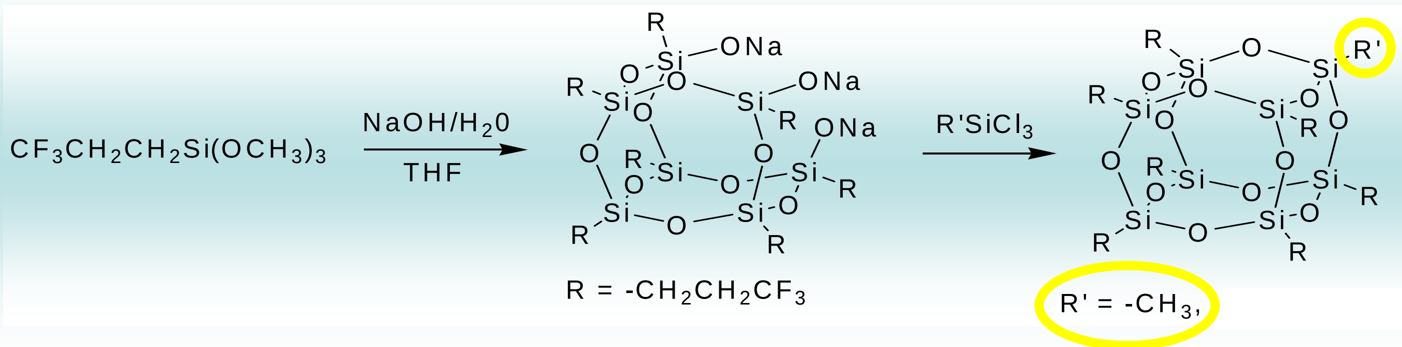


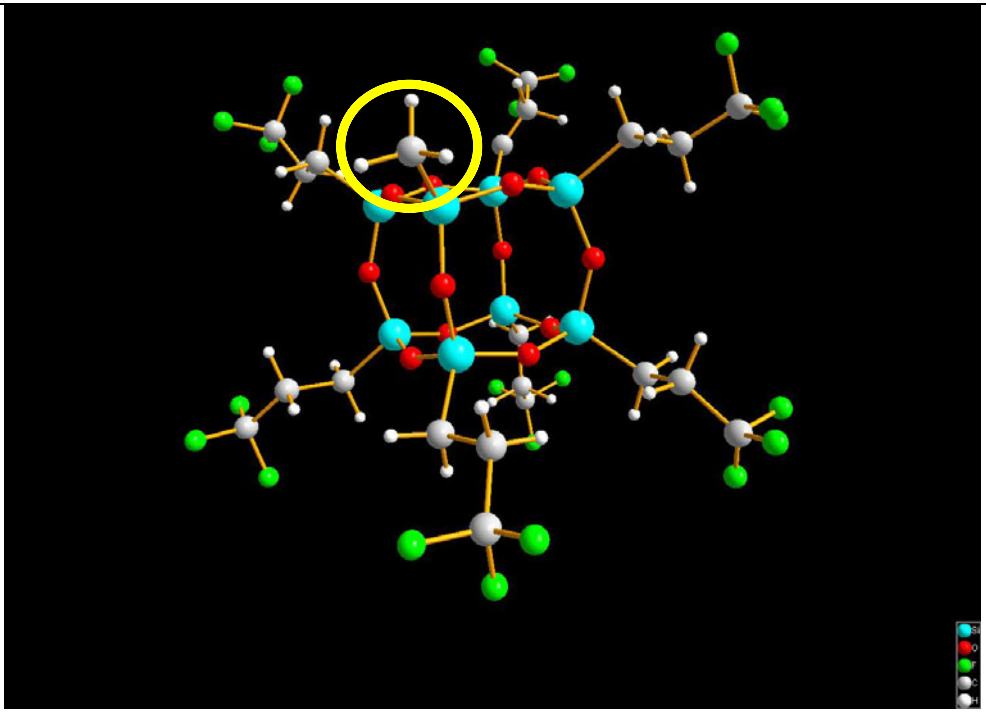
Proton ratio 1:1

13C NMR Trifluoropropyl POSS

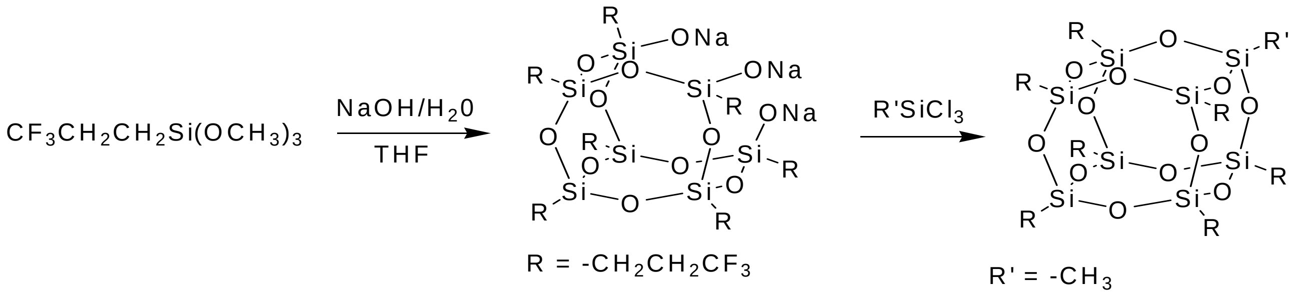


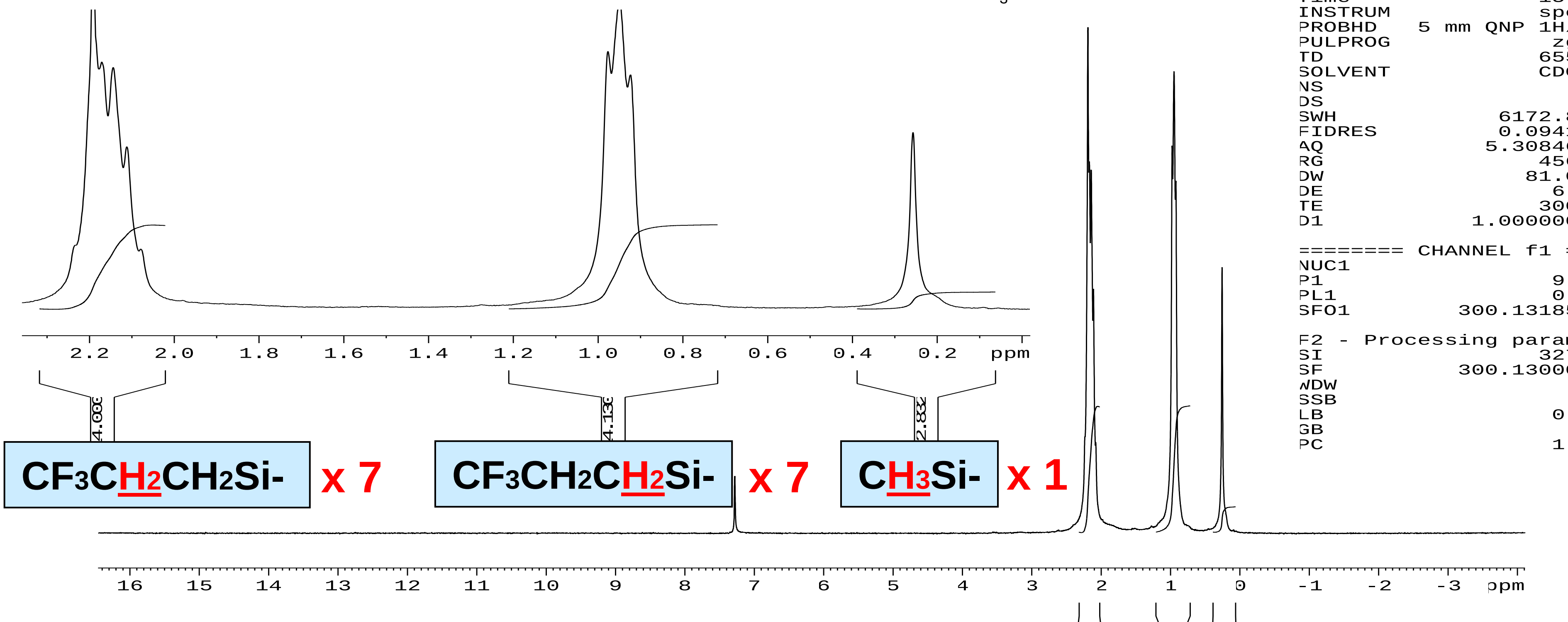
Me corner-capped Fluoropropyl T_8 POSS





Me corner-capped Fluoropropyl T_8 POSS

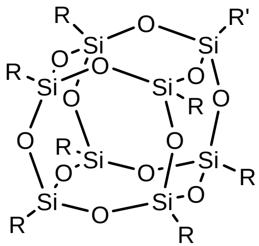


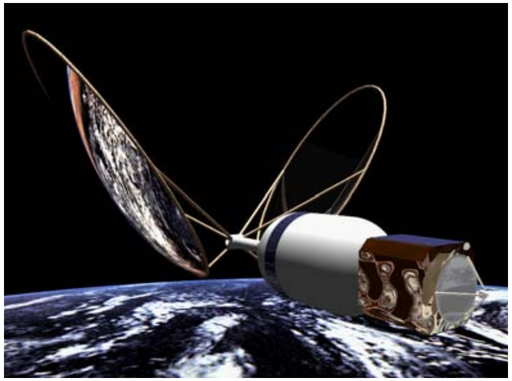


Proton ratio 14 : 14 : 3

Conclusions

- Conventional base catalyzed synthesis yields cage mixtures of fluoro-POSS
  - Redistribution method converts cage mixtures to pure T_8 POSS
- Fluoropropyl POSS does not readily convert to pure T_8 POSS as longer chained fluoro-POSS do
  - New synthetic corner-capping method produces pure T_8
- NMR and x-ray data determined that the new method was a success





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Dr. Sandra Tomczak
Mrs. Tini Vij
Dr. Darrell Marchant
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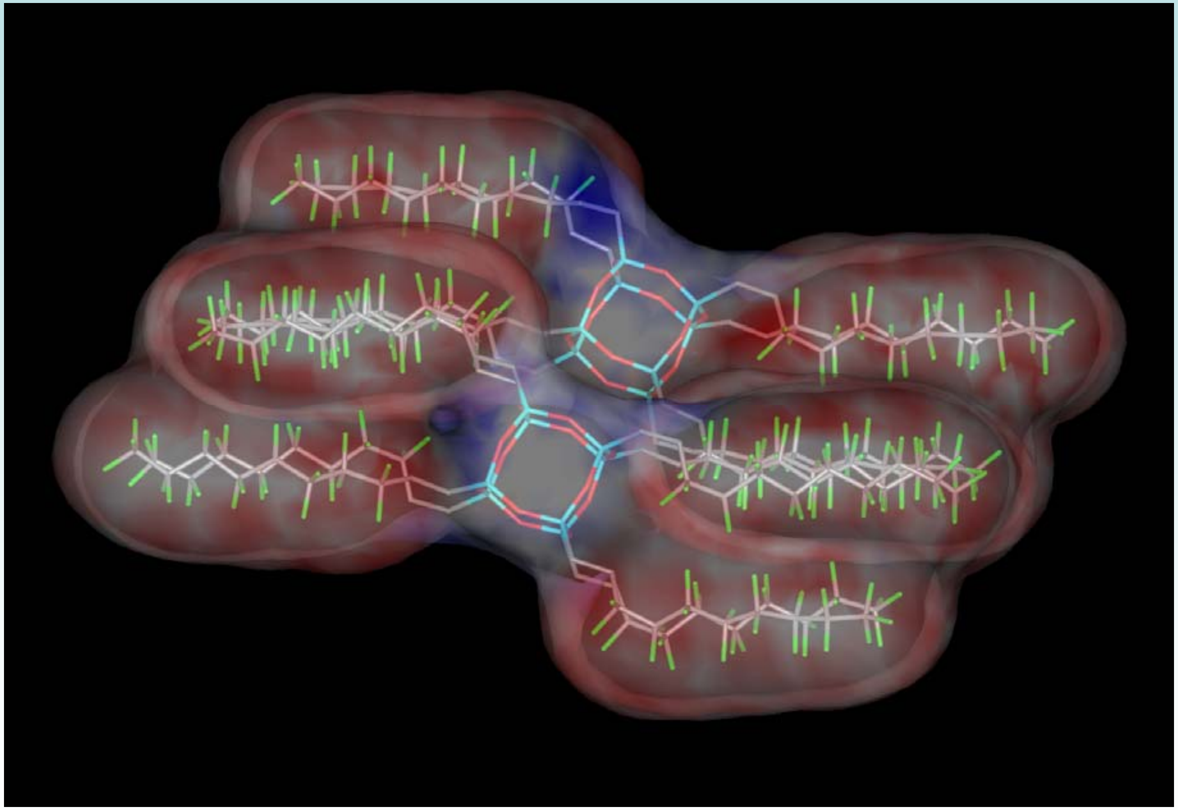
Mrs. Sherly Largo
Dr. Tim Haddad
Lt. Will Cooper
Dr. Rusty Blanski
Lt. Laura Moody
Mrs. Sarah

AFOSR, PRS

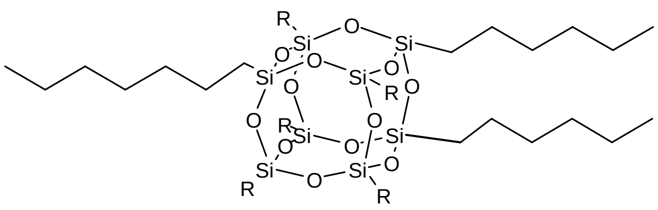
AFRL Fluoropolymer Team



Joe Mabry
Ashwani Vij
Darrell Marchant
Scott Iacono
Tim Haddad
Laura Moody
Jerry Boatz
Pat Ruth
Isha Vij

AFOSR
AFRL/PRSM
AFRL/PRSP

POSS polymer incorporation



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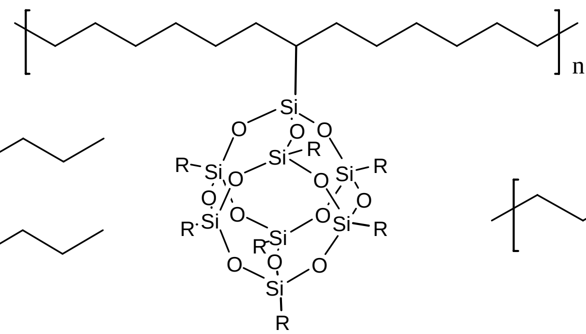
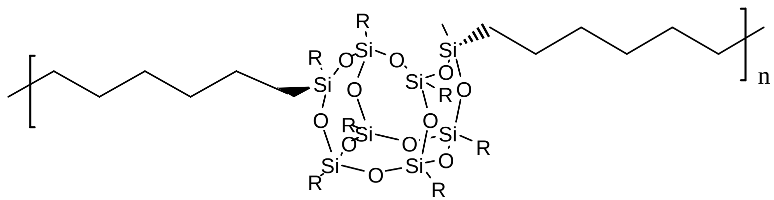
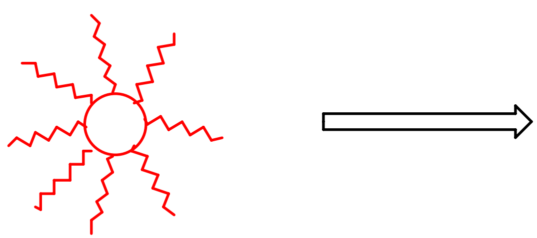
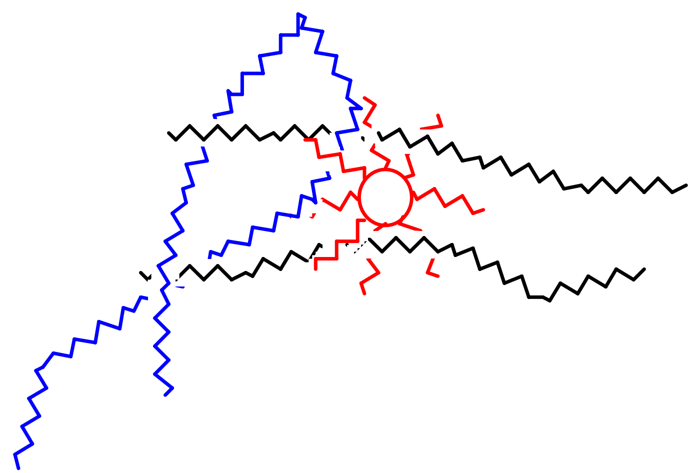


Pendant Polymer



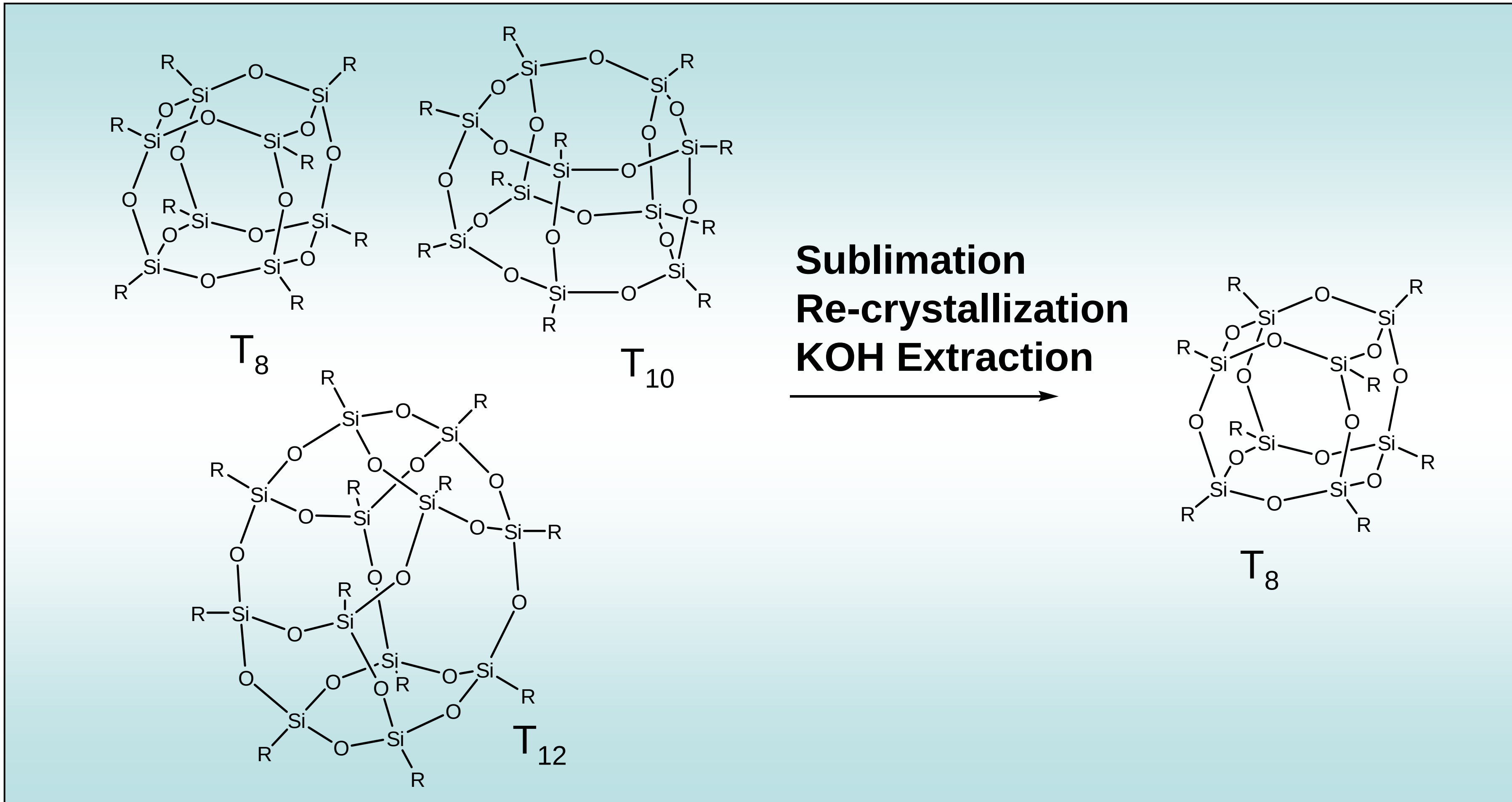
Bead Copolymer





POSS Blending

Redistribution reaction



Abstract

- Abstract
  Fluorinated polyhedral oligomeric silsesquioxanes (POSS) are under investigation for potential lubricant applications. POSS compounds are characterized by a rigid, inorganic core consisting of silicon and oxygen, offering properties similar to those of ceramics; in addition to organic functional groups protruding from the inorganic core, offering organic functionality. Synthesis of POSS generally yields cage mixtures giving varying confirmations of the POSS (Si-O) core denoted by the number of silicon atoms present with T8 being the most abundant conformation. Synthesis of trifluoropropyl-POSS is an exception to this generalization which adopts a preferred T10 conformation, with a minor amount of T8 and T12 isomers. Herein, we describe an alternate synthetic route for the preparation of pure T8 trifluoropropyl-POSS not possible by conventional methods. The POSS cages are characterized by multinuclear NMR as well as low-temperature, single crystal x-ray diffraction studies.